Supporting Information:

Positioning energy levels of photocatalytic powders combining UPS and UV

spectroscopies

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TiO₂ size estimation by XRD:



Figure S1: XRD diffraction patterns for the anatase phase (CristalACTiVTM PC500) (A) and for the rutile phase (Rutile US Research Nanomaterials) (B) Peaks marked with the crystallographic plane in red are those used to estimate the crystal size.

Size for both TiO2 phases was estimated with the Scherrer equation. With $\lambda = 1.5406$ Å and β instr. = 0.06 ° Crystal size was around 7 nm for the anatase and around 25 nm for the rutile.

UPS calibration with a clean Ag foil as a reference

UPS is a three-step process guided by a kinematics photoemission routine. Photogenerated electrons must travel to the surface, to be finally ejected into the vacuum. An analyzer collects them by a finite acceptance angle measuring their kinetic energy E_{kin} .¹

During the travel to the surface, a part of the electrons are submitted to the inelastic collisions inducing thus changes in the E_{kin} . Therefore, two kinds of electrons are collected, primaries without any inelastic interaction and secondary electrons (SE) with loss of energy. SE appears at low E_{kin} with a sharp cut-off, which corresponds to the electrons having just enough energy to leave the sample. They are used to calculate the sample work function Φ_s using eq.1:

$$\Phi_{\rm s} = h\nu - |E_{\rm F} - E_{\rm cutoff}| \tag{1}$$

However, the analyzer also has a work function (Φ_a). Electrical connection between the analyzer and the sample, through the sample holder induce a contact potential of $\Phi_s - \Phi_a$. And thus:

$$E_{kin} = h\nu - E_b - \Phi_s + [\Phi_s - \Phi_a] = h\nu - E_b - \Phi_a$$
⁽²⁾

Plus, electrons incoming in the analyzer can also create secondary electrons. To overcome those issues, an accelerating potential (E_{acc}) is applied to separate the secondary edges of sample and analyzer :

$$E_{kin} = hv - E_b - \Phi_a + E_{acc}$$
(3)

 E_{acc} is adjusted with a standard sample, a cleaned Ag foil. The bias of -9.12 V was choosen to get a work function for the silver close to 4.3, the expected value.² (See Figure S2.A). Emission bands between 4 and 8 eV are mainly related to the d-band of the silver.

Ag foil was first chemically cleaned outside of the analysis chamber and then cleaned by ion gun inside. It is first clean by ion gun during 15 min at a power of 4 keV. The induced current is around 5.4 μ A with a P_{Ar} = 7.0 10⁻⁷ torr. Decreasing of O 1s, C 1s and other impurities signal indicates the surface is sufficiently cleaned by the above procedure. (See Figure S2.B). On the contrary intensity of the Ag 3s, 3p and 3d states is increased. A second ion gun cleaning can be made if the result was not satisfactory.

The intrinsic resolution is determined by analyzing the width of the Ag Fermi level edge. First, a scan with a lower step was acquired (See Figure S2.C). Three lines are drawn on the spectra, the width between the two intersections gives the intrinsic resolution for the silver, measured by UPS. It is estimated to be 0.17 eV.³ A second method, reported by Reinert et al. is also used and provides a resolution of 0.23 eV. From those results, we can conclude that the resolution of the apparatus is close to 0.2 eV.



Figure S2.(A) Full He I UP spectrum of the clean Ag foil (black) and its first derivative (red). Spectrum was acquired with a pass energy of 20 eV an acquisition step of 0.05 eV and a dwell time of 200 ms. (B) XPS spectra of the Ag foil before (black) and after (red) the ion gun cleaning at 4 keV. (C) Graphical determination of the intrinsic resolution. He I UP spectrum of the clean Ag foil at the Fermi edge with the method reported by Schalf et al.³ (red) and the one reported by Reinert et al.¹ (blue).

UPS Spectrum of ITO alone



Figure S3: Full UP spectrum of a commercial ITO/glass substrate chemically cleaned (black) and its first derivative (red). Spectrum is acquired with a pass energy of 20 eV a step of 0.015 eV and a dwell time of 200 ms.

Background treatment

The intensity of the measured spectrum will be noted Itot, the one of the background Iback and thus, the signal (Isignal) will be calculated using:

$$I_{signal}(E) = I_{tot}(E) - I_{back}(E)$$

The background developed by Li et al.⁴ is an improvement to the integral background function. It was developed specially for the fit of low binding energy area. It takes into account the creation of secondary electrons by primary ones, a non negligible phenomenon in the energy area. This background depends of two parameters: Emax, the energy above which the signal is close to zero and Emin, the energy below which the spectrum is only composed of the background.

$$I_{back}(E) = I_{tot}(E_{max}) + \left[I_{tot}(E_{min}) - I_{tot}(E_{max})\right]_{E_{max}}^{E_{max}} \int_{E_{max}}^{E_{max}} I_{tot}(E') - I_{tot}(E_{max}) dE'$$

To show the accuracy of this background it was compared with a Tougaard one. It permits to compare a valence band dedicated background (Li background) with a core level type background (Shirley, Tougaard) (Figure S4. A). After normalization, both resulting spectra are plotted on Figure S4. B. Trend are very different, that is why background subtraction must be done carefully. Figure S4. C shows the decomposition of the UP spectrum after a Li background subtraction. Same methodology is followed after a Tougaard background subtraction and Figure S4. D compares the different contribution of the initial spectrum. A Tougaard background seems to underestimate the contribution of the two first peaks at 4.7 eV and 5.9 eV. That is why, it is more appropriate to subtract a background dedicated to the valence band.



Figure S4: (A) He I UP spectrum of the TiO₂ on ITO sample, prepared by heptane deposition method (black). In red and blue the $I_{background}$ from Tougaard and Li, respectively. Background were calculated between 12.5 and 0.0 eV. (B) Resulting I_{signal} from the background substraction of Tougaard (red) and Li (blue). Two spectra were normalized with the peak around 8 eV. (C) He I UP spectra of the anatase/ITO after a Tougaard background substraction (black line). Spectrum is decomposed in four contribution as reported on Figure 1 (red, blue, green, yellow lines) and leads to the fit result (black squares). (D) Area under the different contribution for the two backgrounds discussed, Li in blue and Tougaard in red.





Figure S5: (A) He I UP spectrum of the TiO₂-anatase on ITO sample, prepared by the drop of a TiO₂-heptane suspension. (B) He I UP spectrum of the TiO₂-anatase on ITO sample, prepared by the drop of a TiO₂-pentane suspension. Black lines corresponds to the wide spectrum acquired with a pass energy of 20 eV a step of 0.025 eV and a dwell time of 200 ms. Red lines correspond to a zoom of the low binding energy acquired with a lower step (0.015 eV). Black and red squares are the first derivative of the corresponding spectra. They gave the $E_{cut-off}$ and the E_{VB} with an accuracy of ± 0.1 eV.





Figure S6: (A) He I UP spectrum of the TiO₂-anatase on ITO sample, prepared by EPD method. (B) He I UP spectrum of the TiO₂-rutile on ITO sample, prepared by EPD method. Black lines corresponds to the wide spectrum acquired with a pass energy of 20 eV a step of 0.05 eV and a dwell time of 200 ms. Red lines correspond to a zoom of the low binding energy acquired with a lower step (0.02 eV). Black and red square are the first derivative of the corresponding spectra. They gave the $E_{cut-off}$ and the E_{VB} with an accuracy of ± 0.1 eV.

Table S1: Comparison of the E_{VB} position between the 2nd derivative method advocate in this work and the so-called intercept method i.e energy position of the intercept of a straight line fit the valence band decay and the x-axis reported in the literature. ^{5,6}

	E _{VB} anatase (eV)	E _{VB} rutile (eV)	$\begin{array}{c} \Delta E_{VB} \\ (eV) \end{array}$	E _{CB, abs.} anatase (eV)	E _{CB, abs.} rutile (eV)
Intercept method	3.5	3.1	0.4	-4.55	-4.3
2 nd derivative method	2.9	2.5	0.4	-3.95	-3.7

The valence band edge follows a Fermi Dirac distribution. At room temperature, the Maxwell Boltzman approximation can be used. The linear extrapolation of the resulting exponential may induce a lack of information for the energy for which the signal increases of few percent.

As is commonly known for the photochemical processes, it is the electrons at the edge of the valence band that are involved. The method to determine the E_{VB} must take them in account. That is why, we proposed the 2nd derivative method to determine the inflexion point i.e. the energy for which the first electrons can be photoexcited.

Absolute UPS measurement



Figure S7: He I UP spectrum of the TiO_2 -anatase on Ag substrate, prepared by the drop of a TiO_2 -heptane suspension (green). UP spectrum of the clean Ag foil (blue). UP spectrum of the TiO_2 -anatase on ITO substrate, prepared by the drop of a TiO_2 -heptane suspension (Figure S5A) (red).

Ag foil was not fully covered by the TiO₂-based suspension on purpose. UPS spectrum shows, therefore, both contributions of the Ag foil and of the TiO₂. A reminiscent d-state and the Fermi level of the Ag foil are observed at -10.4 eV as well as the third state of the TiO₂ signature (See Figure S7). No energy adjustment was required to overlay the spectra suggesting the absence of a measurable band alignment between the Ag foil and the deposited powder of TiO₂. As the work function of the Ag foil is known eV ($E_{FL,Ag} = -4.2 \text{ eV}$) all the spectra can be plotted in absolute energy. Finally, valence band maxima is determined relatively to the vacuum level, $E_{VB} = -7.1 \text{ eV}$.

UV-vis absorption measurements:



Figure S8: (A) UV-vis absorption spectra for TiO₂-anatase diluted with BaSO₄ at different mass ratio: $1:40^3 = 16$ ppm (black), $1:40^4 = 0.39$ ppm (blue), $1:40^5 = 0.0098$ ppm (red) (B) UV-vis absorption spectra for TiO₂-rutile diluted with BaSO₄ at different rate: $1:40^4 = 0.39$ ppm (blue), $1:40^{4.2} = 0.19$ ppm (green), $1:40^5 = 0.0098$ ppm (red).

The absorption coefficient is obtained from the previous Kubelka-Munk plot, as followed, and permits to determine the band gap for anatase and rutile with a Tauc plot:

$$F_{KM} = \frac{k}{s} = \frac{\left(1 - R_{\infty}\right)^2}{2R_{\infty}}$$

 $\frac{F_{KM, sample}}{F_{KM, standard}} = \frac{\frac{k_{sample}}{s_{sample}}}{\frac{k_{sample}}{s_{standard}}} \approx \frac{\frac{k_{sample}}{s_{standard}}}{\frac{k_{standard}}{s_{standard}}} = \frac{k_{sample}}{\frac{k_{sample}}{k_{standard}}} \approx k_{sample}$

After smoothing the spectra we can determine band gap using Tauc's relationship⁷ for indirect semiconductors (Figure S9):

$$(\alpha h\nu)^{1/2} \propto (h\nu - E_g)$$

With α the absorption coefficient and $h\nu$ the photon energy. The intercept between the linear part of the curve $(\alpha h\nu)^{1/2} = f(\alpha h)$ with the x-axis is E_g. A band gap of 3.0 ± 0.05 eV was determined for rutile. However, two linear parts are observed for anatase; it is a phenomenon due to phonon participation, reported by Würfel and Würfel.⁸ The following equation must be used to determine Eg, with E_p the phonon energy:

$$(\alpha)^{1/2} \propto (h\nu - E_g \pm E_p)$$

The two intercepts between the linear part of the curve with the x-axis provide $E_g + E_p$ and $E_g - E_p$. The mean value corresponds to $E_g = 3.15 \pm 0.05$ eV.



Figure S9: (A) Plot of $(\alpha hv)^{1/2}$ versus photon energy for rutile diluted with BaSO₄ (0.19 ppm). (B) Plot of $(\alpha)^{1/2}$ versus photon energy for anatase diluted with BaSO₄ (0.39 ppm).

The normalized spectra "t (hv)" were fitted with normal distributions as follows, using μ which corresponds to the position peak, σ its standard deviation and I_i . Those parameters are reported in table S2 and S3.

$$t(h\nu) = \frac{I_i}{\sigma\sqrt{2\pi}}e^{-\frac{(h\nu-\mu)^2}{2\sigma^2}}$$

Table S2: Parameters I_i , μ and σ used to obtain the fit reported on Figure 4. (A) Fit was obtained using a least squares method.

	α	β	γ	δ
I _i x 10 ³	1.97	5.55	7.18	3.42
μ (eV)	4.1	4.5	5.0	5.4
σ (eV)	0.24	0.26	0.26	0.25

Table S3: Parameters I_i , μ and σ used to obtain the fit reported on Figure 4. (B) Fit was obtained using a least squares method.

	3	α	β	γ	δ
I _i x 10 ³	1.61	1.95	1.69	5.22	10.8
μ (eV)	3.7	4.3	4.6	5.1	5.7
σ (eV)	0.27	0.21	0.18	0.24	0.28

Table S4: Position and full width at half maximum (FWHM) of the contribution under the UPS spectra of Figure 5. The binding energy (BE) is relative to the silver Fermi level ($E_F = -4.2 \text{ eV}$). The absolute position of each peak is therefore obtained as follow: $E_{abs} = -BE - E_{F,Ag}$

	Anatase				Rutile			
	Ι	II	III	IV	Ι	II	III	IV
Binding Energy (eV)	4.85	6.0	8.1	10.8	4.5	5.8	7.8	10.6
Absolute position (eV)	-9.05	-10.2	-12.3	-15	-8.7	-10.0	-12.0	-14.8
FWHM (eV)	1.3	1.9	2.8	1.2	1.6	2.0	1.9	1.2

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